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Nonlinear Optics and Organic Materials

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# Organic materials for nonlinear optics

Part 1

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Elizabeth Cavicchi  
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In glancing through a flat windowpane we confront light's interaction with glass, but ignore it. We assume that the world's image is not perceptibly altered when light passes through the glass. Yet glass does play tricks with light: A penny viewed through a variety of lenses may appear the same size, magnified, reduced, or blurred. The shape of glass dictates the distortion of the image. The 14th century craftsmen who first formed lenses from glass to aid those with deteriorating vision progressed by trial and error. Even Galileo used the exacting labor of grinding glass, without benefit of a practical theory of optics, to improve his pioneering telescope. The optics industry flourished for centuries before theory could minutely chart the interaction between light and glass.

Contemporary optics research is distant from common experience, seeking clues far more subtle than the shape of a piece of glass, with techniques more esoteric than abrasive polishing of a glass lens. The traditional dominance of glass in optics is now challenged by a host of synthetic materials that exhibit unusual optical behavior. Laser light of unmatched brilliance both probes and incites these novel effects. A detailed understanding of the nature of light, and how it interacts with matter, is essential to evince these effects. Although everyday optical tools—windowpanes and eyeglasses—may remain unaffected, such delicate engineering has thrust optics along routes far removed from the crudely empirical development of geometrical optics.

In this paper we will follow some of the newly laid routes into the domain of organic materials—materials that have such unusual responses to light that they undermine some of our intuitive assumptions about optics. The molecular structure of these organic materials can be custom designed to amplify their optical properties. Novel devices based on the optical phenomena manifested by organic materials may change communications and information processing.

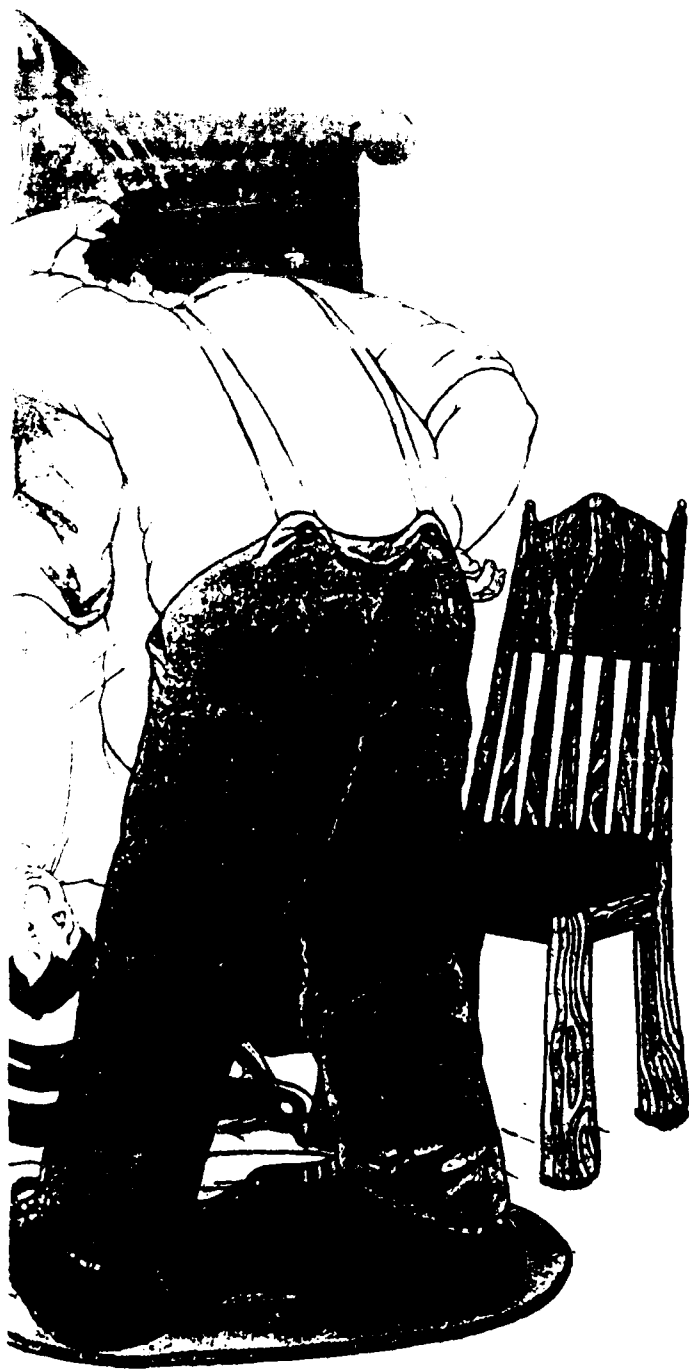
## Refraction and linear optics

Both familiar and novel optical properties of materials depend intimately on the character of light. A beam of light can be simply modeled as a stream of many packages, all moving in a straight line at the same speed. Each package, or photon, is a self-propelled carrier of energy

and momentum. The package is composed of a pair of perpendicular electric and magnetic field vectors whose magnitudes and directions oscillate periodically. The frequency of this oscillation dictates the "color," momentum, and energy content of the package; higher frequencies correspond to greater energy and momentum. The oscillations of the electric and magnetic fields are in phase if their magnitudes peak simultaneously. If the peaks are asynchronous, the electric vector cancels and the light disappears.

When light in air enters a denser, transparent material such as glass, its electric field induces a slight separation





between the positive and negative charges on each molecule in the material. Negative charges attempt to orient toward the instantaneous positive direction of the field of light, and vice versa. The dielectric constant,  $\epsilon$ , is a measure of this response of charges in a material to an applied electric field (usually dc). A small electric field, which reflects the spatial arrangement of the molecules, is created by the polarization of charge. Its direction opposes the incident field; it oscillates asynchronously with light. This small electric field, induced by light, in turn alters the direction and diminishes the magnitude of the field of light. As a consequence, the speed of light is reduced

within the material. The fields of light perturb charges in the material, which in turn perturb light through an induced field. Although this interaction occurs microscopically, it has a familiar macroscopic effect: refraction. When a pencil partially immersed in water appears crooked or a lens focuses a bright spot of light, we observe refraction.

The index of refraction,  $n$ , is the ratio of the speed of light in free space to its speed in a material. The value of  $n$  is characteristic of the material. Although light of all "colors" travels at the same speed in free space, its speed inside a material varies slightly with color, or frequency; the index of refraction is frequency dependent. A prism sorts white light into a rainbow by deflecting the higher frequency, bluer "colors" farther from the path of the incoming beam. When the frequency of light approaches one of the material's built-in natural frequencies, the molecules oscillate sympathetically, absorbing more of light's energy. Ordinarily, the index of refraction of a material is not affected by the brightness of the light shining on it, a quality that enables us to use the same pair of binoculars to focus on a faint star at night and a bird in daylight (1, 2).

#### Intensity-dependent nonlinear effects

However, when laser light is directed on a material, entirely different properties—microscopically sensitive to a precise match between light and the material—can be evoked. The high intensity of a laser beam can produce an electric field that rivals and disrupts the internal electric field of atoms in the material. The closely correlated oscillation phases, or coherence, of a laser beam produce a well-defined field pattern, persistent in space and time. This can evoke complex, collective behavior in an ordered material system. Through interaction, light and the material can drastically alter each other in a uniquely interrelated fashion.

In conventional circumstances, when two light beams cross each other the departing photons in one beam appear unaffected by the other beam. But if two light beams coincide while traversing certain special materials, the departing photons may become distinguishable from the incident photons. The first beam alters the material's optical behavior; the second beam, arriving while the

**Table 1. Second-order nonlinear optical properties\***

Material	$n$	$\epsilon$	$d_i \times 10^{-12}$ m/v
KDP ( $\text{KH}_2\text{PO}_4$ )	1.47	42	$d_{36} = 0.45$
LiNbO <sub>3</sub>	2.3	78	$d_{22} = 2.3$ $d_{33} = 40$
MNA (2-Methyl-4-nitroaniline)	1.8	4	$d_{11} \sim 250$
DANS (4- <i>N,N</i> -dimethylamino-3-acetamionitrobenzene)	1.71	4	$d_{eff} \approx 27$

\*  $n$  is the real part of the index of refraction,  $\epsilon$  is the dielectric constant,  $d_i$  is a second-order nonlinear coefficient in the direction  $i$ .

influence of the first is still in sway, "sees" a different material. Its future course diverges from that observed in the absence of the first beam. Once the optical field has departed, the material gradually reverts to its unperturbed state. The duration of this relaxation is the material's characteristic response time. A light beam emerging from such an interaction is often qualitatively changed (e.g., in frequency or intensity) or refracted from the incident beam. This behavior is termed nonlinear optics; the input and output beams cannot be related by a simple proportionality (3).

A myriad of events occurring at the intimate scale of local interaction between light and the material can induce large-scale nonlinear effects. The electric field of the laser beam can contort the shape of atoms by drawing the electrons toward its direction or by inciting electrons to jump to a different electronic orbit. The arrangement of atoms in the three-dimensional matrix of the material can shift, as the field pulls oppositely on the positively and negatively charged atoms. The field can induce an array of randomly oriented molecules to align uniformly along its direction. Bonds between atoms can be stretched or even broken by the electric field. If the beam's intensity is increased, its electric field also increases, evincing more pronounced distortions in the material. Yet a twofold increase in light intensity will not induce a twofold increase in distortion. The extent of distortion is contingent upon the material's inherent electronic properties. Any disruption of the charge configuration of the material will be macroscopically observable as a change in the speed and refraction of light.

A century ago researchers found that strong electric fields could alter the optical properties of materials. Ordinarily, glass is isotropic: It exhibits the same refraction no matter what the angle of incident light. Kerr showed that the refraction of light passing through glass along the direction of an applied electric field is different from the refraction along a perpendicular (4). Pockels discovered the same behavior in crystals that lack a center of symmetry (5). However, it was not possible to use the electric field of light to change the way materials refract light—until the laser was invented.

Light-induced optical effects can be more dramatic than the processes observed by Kerr and Pockels. An

intense laser beam can induce a discontinuity in the way the material—both within and outside the beam's path—refracts light. This discrepancy, for example, may create a lens that is embedded in the material and that focuses the beam to a remarkable bright, narrow spot. The energy of the laser beam, focused by the lens to a point, can even damage the material. In optical fibers, uncontrolled "self-focusing" of light, caused by the nonlinearity of the materials, can disrupt both the transmission and the fiber.

### Optical harmonics

The seminal experiment in nonlinear optics was conducted by Franken in 1961 (6). A beam of red light from a ruby laser was directed through a quartz crystal, and the light emerging from the crystal included both a red and an ultraviolet component. Franken found that the frequency of the UV component was precisely double that of the incoming red light. This doubled frequency is called the second harmonic, in analogy with acoustics, where the higher harmonics of a fundamental tone are integer multiples of the frequency of the fundamental. The rich quality of musical sound derives from the simultaneous vibration of an instrument's string or air column at the fundamental and its harmonics; however, the world would look quite different if optical harmonics were commonplace. Light photons ordinarily do not interact with each other to change frequency. White light that passes through a piece of blue glass appears blue only because the glass absorbs all but the blue light; the glass did not transform photons from one "color" to another.

In the year following Franken's discovery, Bloembergen explicitly derived these optical effects by incorporating perturbing motions of electrons and charged atoms into the quantum mechanical model of light's interaction with matter. His study became the theoretical foundation of nonlinear optics, for which he was awarded a Nobel Prize in 1981 (7, 8).

A material exhibiting optical nonlinearities can override the noninteracting nature of photons. The material mediates the interaction; the energies of two incident photons may be added, producing a new photon at the combined energy. When the new photon is released, the difference in momentum between the incoming and the outgoing photons may be absorbed by the matrix of the material. If two laser beams of different frequencies impinge on a material, a light output of more diverse frequencies is possible. A material interacting with photons of unequal energy may emit that energy either in a single photon at the total combined energy or as several photons that split the total energy between them. The material facilitates these transformations without being affected itself; it acts as a catalyst.

When photon energies are combined to create photons of a new color, the refractive speed of the light beam



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Table 1. Second-order nonlinear optical properties<sup>a</sup>

Material	$n$	$d$ (10 <sup>-12</sup> )	Response time, s
GaAs (100)	3.20	14.1	<10 <sup>-12</sup>
LiNbO <sub>3</sub>	2.43	1.0	<10 <sup>-12</sup>
CS <sub>2</sub>	1.59	1.1	<10 <sup>-12</sup>
Fused silica	1.46	0.0095	~10 <sup>-14</sup>
PTS polydiacetylene	1.88	80.0	~10 <sup>-14</sup>
MNA	1.8	25.0	~10 <sup>-14</sup>
p-Nitroaniline	—	14.0	~10 <sup>-14</sup>

<sup>a</sup>  $d$  is a measure of the intensity-dependent index of refraction.

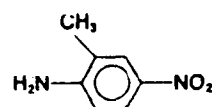
changes, for the speed depends on frequency. The incident and resultant beams each travel at different speeds because of their different frequencies. At its creation, each new photon oscillates in phase with its parent photons. However, because the pace of the child beam differs from its parent, the oscillation phases of photons emitted by widely separated atoms will fall out of synchronization. These out-of-phase oscillations will cancel, diminishing the intensity of the new beam. For optical harmonics and mixture frequencies to be observable, the material's refractive properties must be manipulated to prevent phase cancellation. Sometimes by either heating or rotating the material, the speed of the incoming light traveling along one direction can be matched to that of the outgoing beam, traveling along a perpendicular. Then the phases of the newly created photons will remain synchronized. An even more stringent condition governs the combination of two photons with different frequencies to produce a third, or more. If the speeds of all three beams are not matched, phase cancellation will negate the effect (9-11).

#### Materials and nonlinear optics

Light and material must be tailored to precisely complement each other before these unusual effects can arise. The electric field of light interacts with and disrupts the electrical environment internal to the material. By systematically tweaking the molecular structure of a material, its interaction with light can be analyzed. Insights derived from these studies of light and matter can shape the design of new materials with an enhanced nonlinear response to light.

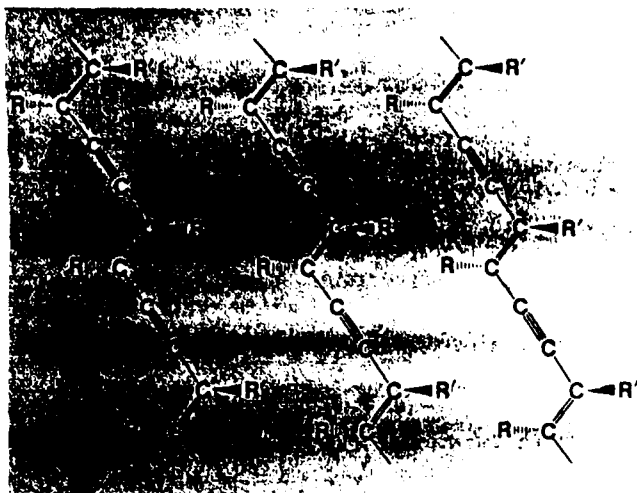
The detection of nonlinear optical behavior in ordinary materials is elusive; ideally the material must possess superior optical quality—transparency, freedom from defects that scatter light, uniformity, a polished surface—in addition to sustaining the matching of light's refractive speeds. Inorganic materials traditionally associated with optics (e.g., quartz and the new semiconductors) initially received the most attention. For example, lithium niobate, which can be grown as single crystals, satisfies many of these criteria; however, further enhancement of these properties is desirable. Several organic materials match and may even exceed the efficiency of lithium niobate in generating optical harmonics. However, deficiencies in other properties such as phase-matching ability may hinder their practical use (12).

Results of some comparative studies of the nonlinear optical behavior of inorganic and organic materials are summarized in the two tables. Table 1 lists parameters relevant to the production of second-order optical harmonics: the index of refraction,  $n$ ; the dielectric constant,  $\epsilon$ ; and a directionally dependent measure of the second-order effect,  $d$ . Materials with a high  $\epsilon$  respond sluggishly to the stimulus of light's electric field. In this respect, 2-methyl-4-nitroaniline (MNA)

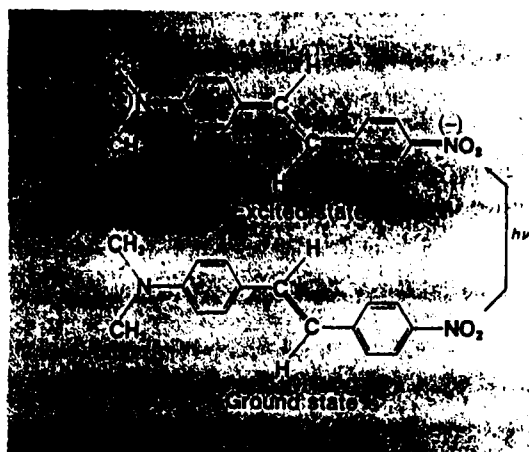


with a 5% lower dielectric constant and a 100-fold higher second-order coefficient than lithium niobate, would be preferable for applications in which a quick response time is critical to the operation of a device. (We will describe the nature of these devices in Part 2 of this series.)

Table 2 gives characteristics pertinent to the third-order harmonics: index of refraction,  $n$ ; a third-order index,  $n_3$ ; and the response time. Again the organic materials excel both in rate of response and in magnitude of the third-order effect. Inorganic materials typically must compensate for changes in their electrical environment by shifting the position of atomic nuclei, a slower process than the electronic motions that perform the same function in organics. The inherently rapid electronic perturbations in organics—orders of magnitude faster than switching times in electronic devices—have potential for inclusion in information processing systems. The optical and electrical properties of a material proceed directly from the identity of its component parts—atoms and molecules—and from the arrangement of these parts into a superstructure. Inorganic materials constitute a limited range of atomic species; improvement of nonlinear performance must be sought through a change in crystal structure rather than by subtle modifications to the molecule. This is a daunting prospect, for the material may exist only in a specific crystal form. Even if other structures exist, the effort to grow a new form of crystal is typically laborious and protracted. Organic molecular structure, however, can be modified incrementally by making small changes in the backbone or substituents. In this way the chemist can fine-tune the material's response to light as well as its other chemical and mechanical properties.



**Figure 1.** Polydiacetylene chains in a crystal. R is an electroactive side group and R' is a surfactive group



**Figure 2.** Molecular structures of the ground and resonance excited states for 4-dimethylamino-4'-nitrostilbene (DANS).  $N(CH_3)_2$  is the electron donor and  $NO_2$  is the electron acceptor

A conjugated backbone appears to be crucial to the ability of polymeric molecules to generate third harmonics. The  $\pi$  electrons, distributed along the backbone, react quickly when the electrical environment is changed by another molecule, an electric field, or light. This quick response and the extensive spreading of the  $\pi$  cloud is the source of a sizable, fast, third-order response in these quasi one-dimensional systems.

The polydiacetylene class of polymers has emerged as one of the more promising prospects for third-order nonlinear effects. The third-order index,  $n_3$ , of polydiacetylenes (Figure 1) is one of the larger indices

demonstrated to hold within the range of the transparent frequencies of a material. The response time of polydiacetylenes is predicted to be in the subpicosecond range (Table 2).

Organic molecules with other nonlinear behavior, such as second-order effects, can be integrated into the diacetylene through the side groups. The  $\pi$  electrons are polarizable along the length of the macromolecular backbone. This extensive conjugation—in the substituents, in the backbone, and in their interplay together—may be responsible for a broad range of nonlinear phenomena not possible in a single monolithic inorganic system. The side groups R and R' can be varied and modified to optimize optical, mechanical, and processing properties (13).

Molecular hyperpolarizability,  $\beta$ , is a measure of the tendency of a molecule to exhibit second harmonics. Two terms contribute to the hyperpolarizability: an asymmetry term,  $\beta_{as}$ , and a charge-transfer term,  $\beta_{ct}$ . A greater asymmetry in the way charge is distributed along a molecule will induce a more pronounced interaction with the electric field of light. Second harmonics, however, will not occur at all if the molecule crystallizes or assembles with a center of symmetry. The charge-transfer term describes the extent to which the field of light induces transitions from the molecule's ground state to its excited, or resonance, state. Because a crystal lattice of organic molecules is stabilized primarily by weak van der Waals forces, its macroscopic second-order behavior can be regarded as an averaged sum of these molecular hyperpolarizabilities.

This correlation between structural and optical properties can be demonstrated by the behavior of 4-dimethylamino-4'-nitrostilbene (DANS) (Figure 2). The  $C=C$ -bridging group confines the molecule to a plane, extending conjugation from end to end and stabilizing its resonance structure. In the resonance structure shown, positive and negative charges are maximally separated, producing a large internal electric field. The electron-donating (dimethylamino) and electron-withdrawing (nitro) groups create an asymmetry in charge. In this case, the charge-transfer term dominates: For DANS the estimated value of  $\beta_{ct} = 3.8 \times 10^{-32}$  esu is very close to the experimental determination of  $\beta_{total} = 4.5 \times 10^{-32}$  esu.

Key parameters extracted from the UV and visible spectrum of DANS confirm these results. The calculated probability of a transition from ground to resonance state (related to  $\beta_{ct}$ ) is very high. In addition, the polarization of the molecule in its resonance state is 4 times greater than in the ground state. This suggests that a molecule that admits a large charge separation in converting to its resonance state will possess a substantial hyperpolarizability. This observation is a possible blueprint for the design of molecules with enhanced nonlinear behavior that may assist in the selection of optimum molecular structures

from the large palette of organic molecular structures available.

Organic materials satisfy other practical requirements for nonlinear optics. They may be selected and tailored to be transparent to light of frequencies convenient for experimentation and applications. In addition, light usually travels at markedly disparate refractive speeds when it is directed along different axes in organic crystals; this phenomenon is termed birefringence. This facilitates the effort to match the phases of the incident beam with the optical harmonic, which is necessary to prevent cancellation of the harmonic (14). Although organic molecules such as DANS can be designed with an asymmetric structure, they often crystallize in a symmetric configuration. This precludes production of second harmonics. Alternative techniques for crystal growth must be devised to circumvent this drawback. A recently developed technique embeds active molecules within a polymer host in which, following alignment in an electric field, they are available for use in nonlinear experiments. This remarkable approach bypasses the stringent demands of crystal growing.

In Part 2 our attention shifts from the theoretical foundations of nonlinear optical behavior in polymers to the more practical agenda of processing these materials and incorporating them into optical devices. The techniques of casting, crystallization, and thin-film multilayer growth are adapted for the production of the

appropriate form of the polymer that retains its nonlinear function. Through the active component of an optical device (i.e., the nonlinear material), a light beam or imposed electric field operates on the incident light by either switching or altering its information content. The emergent light beam bears the imprint of the nonlinear interaction as a change in its frequency, direction, or intensity.

#### References

- (1) Meyer-Arendt, J. R. *Introduction to Classical and Modern Optics*, Prentice-Hall, Englewood Cliffs, NJ, 1984; pp. 18-34, 175-86.
- (2) Baldwin, G. C. *An Introduction to Nonlinear Optics*; Plenum: New York, 1973; pp. 11-69.
- (3) Giordmaine, J. A. *Sci. Am.* **1964**, *210*(4), 38.
- (4) Kerr, J. *Philos. Mag.* **1875**, *50*, 337, 446.
- (5) Pockels, F. C. A. *Neues Jahrb. Mineral.* **1891**, *7*, 201; **1893**, *8*, 407; **1894**, *Bd. 2*, 241.
- (6) Franken, P. A.; Hill, A. E.; Peters, C. W.; Weinreich, G. *Phys. Rev. Lett.* **1961**, *7*(4), 118.
- (7) Bloembergen, N. *Phys. Rev.* **1962**, *127*, 1918.
- (8) Bloembergen, N. *Nonlinear Optics*; W. A. Benjamin: New York, 1965; pp. 121-49.
- (9) Baldwin, G. C. *op. cit.*, pp. 71-107.
- (10) Zernike, F.; Midwinter, J. E. *Applied Nonlinear Optics*; Wiley: New York, 1973; pp. 102-23, 130-39.
- (11) Shen, Y. R. *The Principles of Nonlinear Optics*; Wiley: New York, 1984.
- (12) Zernike, F. *op. cit.*, pp. 73-101.
- (13) Carter, G. M.; Chen, Y. J.; Rubner, M. F.; Sandman, D. J.; Thakur, M. K.; Tripathy, S. K. In *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S.; Zyss, J., Eds.; Academic: New York, 1987; Vol. 2, pp. 85-120.
- (14) Meredith, G. R. *MRS Bull.* **1988**, *13*(8), 24.



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Jayant Kumar is a faculty member in the physics department at the University of Lowell. He has conducted research in atomic physics, solid-state physics, integrated optics, and nonlinear optics at UCLA and Argonne National Laboratory. He holds a Ph.D. degree in physics from Rutgers University.



R. Sai Kumar has been a research associate at the University of Lowell since earning his Ph.D. in polymer science there. His research encompasses the design, synthesis, and detailed characterization of polymer liquid crystals and other specialty polymers.



# Nonlinear optics and organic materials

## Part 2

Sukant Tripathy  
Elizabeth Cavicchi  
Jayant Kumar  
R. Sai Kumar

**H**ow much time left till lunch?

How many miles per gallon this past week?

Before answering one of these questions, you will probably glance automatically at figures imaged on a surface by nonlinear optical phenomena—the liquid crystal display. In many watches or calculators, the screen is made from a thin liquid crystal layer sandwiched between two glass plates. In one display configuration, the inner surface of each glass plate is lined with a transparent conducting grid. Variations in the electrical signal at each point on the grid can reorient the liquid crystal molecules and change their optical absorption. The inexorable progression of digits marking seconds of time is a common visible indicator of the modification of light in a nonlinear interaction with matter. We'll now explore other novel devices based on nonlinear optical behavior of polymers that may eventually proliferate in the everyday components of our culture as has the liquid crystal display.

The invention of the laser has revealed a myriad branching cascade of related optical phenomena whose existence was demonstrated and probed by the laser's superior intensity, coherence, and monochromaticity. The oscillating electric fields of laser light are strong enough to compete with the inherent electric fields of atoms and molecules in a sample. The interaction between incident light and a material perturbs both: light's frequency or direction may be altered, while the atom's electronic cloud may become distorted, creating a charge dipole or even flipping the molecule's orientation in space. The incident light beam is qualitatively distinguishable from the emergent light beam: light has undergone a *nonlinear* interaction while traversing the material.

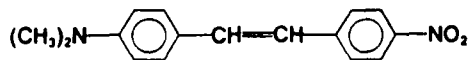
Some organic materials have exhibited pronounced nonlinear optical behavior. These effects appear to be augmented in polymers with a conjugated backbone or with side groups that are susceptible to asymmetric charge polarization under the influence of an external electric field, such as light, among other possibilities. Molecules or side groups with this configuration such as 3-methyl 4-nitroaniline (MNA) are able to sustain a large charge separation between excess positive charge at one end and negative charge at the other end, thus generating a molecular electric field that can, in turn, interact with the field of light. It may be possible to fine-tune the nonlinear

response of a material to advantage in a given application by tinkering with the structure of the polymer in modifying its side groups or backbone geometry. The current interest in organic nonlinear materials derives from this multifaceted potential for molecular "engineering."

### Processing techniques for organic materials

Despite their exceptional nonlinear response to laser light, organic materials have not yet supplanted inorganics such as lithium niobate ( $\text{LiNbO}_3$ ) in applications. The crystalline forms of organic molecules are often characterized by poor mechanical strength and rapid degradation when subjected to radiation and reactive chemicals. Organic polymers, however, are notably resilient, are resistant to environmental degradation, and can be processed into objects of desirable shape. This suggests a research strategy to incorporate active organics exhibiting nonlinear optical properties into polymeric structures, thus synergizing the advantages of both.

In one method of achieving a nonlinear polymer system, the active organic, for example, 4-dimethylamino-4'-nitrostilbene (DANS)



is dissolved in an optically transparent matrix of polymers such as poly(methylmethacrylate) or polycarbonate. This matrix is termed a guest-host material because the active molecule is not chemically bonded with the polymer medium but is only homogeneously dispersed in it (5–10% by weight).

A liquid of a guest-host preparation can be poured onto a mold and solidified by cooling, polymerization, or solvent evaporation, or spin-coated on suitable substrates. In the next step, the thin film produced by either method is heated above its glass transition temperature and subjected to a strong electric field. The active organics align with the field and are frozen in position as the film cools, producing a useful material for nonlinear optics experiments. However, the limited solubility of most active organics in the polymer and their tendency to segregate or migrate out of orientation imposes limitations on the choice of guest-host combinations and their suitability in applications.

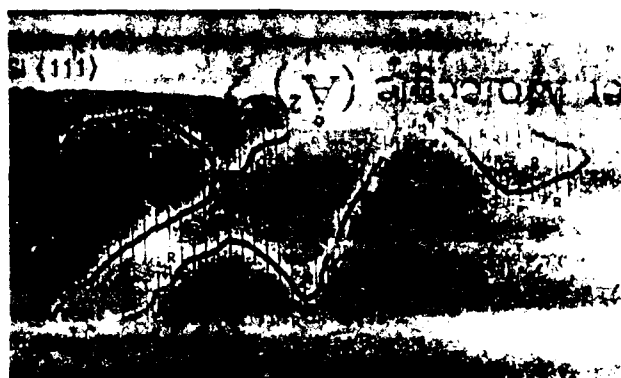


Figure 1. Flexible polymer backbone containing electroactive side groups (R)

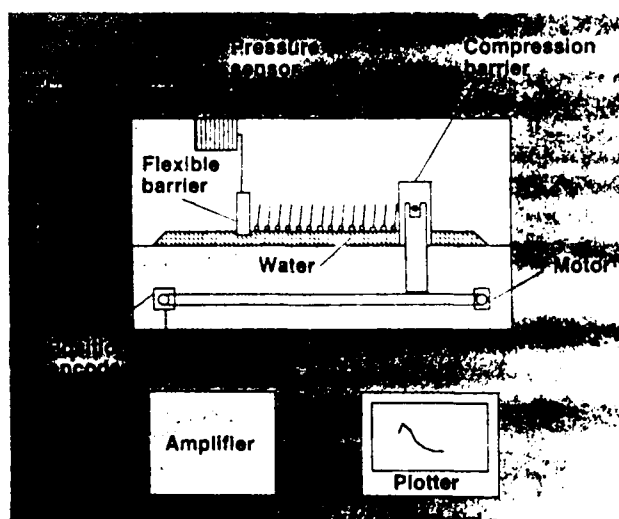


Figure 2. Schematic of Langmuir-Blodgett method

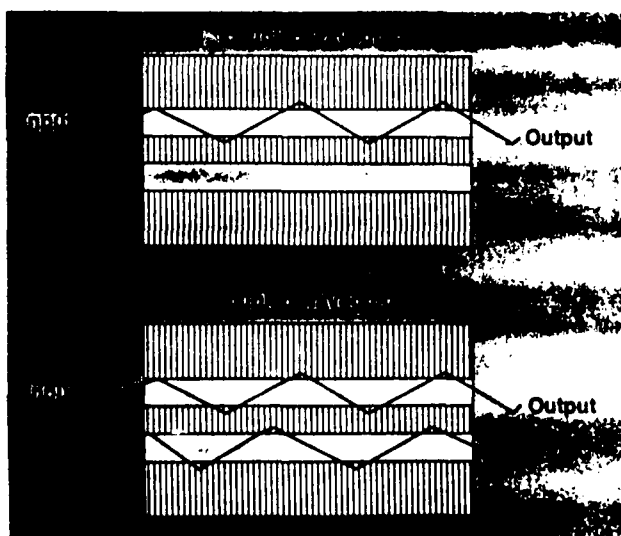


Figure 3. The index of refraction within the waveguide is higher than that of the surrounding shaded material. When two waveguides are coupled, some of the light input at channel A spills over and is output through channel B as schematically shown

In an alternative approach, the active organic moiety may be covalently attached to the polymer backbone, analogous to the teeth of a comb (Figure 1). The polymer backbone may be devoid of nonlinear properties, as in the case of polyethylenes, or it may be made of polydiacetylenes, thus enhancing the material's response to light. Its substituent teeth can be chemically modified following polymerization, allowing the chemist to alter the flexibility. The comb-like structure can be prepared by procedures used with guest-host materials, heated, oriented in a field, and frozen in place.

If the comb teeth are not bulky and are of appropriate shape, the polymer may exhibit liquid crystalline behavior. The charged or polarizable teeth are susceptible to alignment when subjected to suitable fields. The polymer backbone accommodates side group motion through internal rotations of its own. The polymer units may spontaneously align in solution. Subject to application of an electric field or heat will induce reorientation of the polymer chains. The ordering of polymers in liquid crystals is highly anisotropic: backbones along one axis, side chains along another. As a result of this pronounced spatial anisotropy, light directed along different crystal axes travels at different rates. This property of birefringence may assist in achieving conditions appropriate for phase matching.

#### Optical devices

A more intricate tactic is to devise a nonlinear monomer segment that also can be polymerized into a well-organized structure by treatment with heat or radiation. If the monomers are constructed with a head of an active moiety and a polar tail at the other end, the polar tails will align on a water surface, creating a sheet of head-up, active monomers. Just as soap spreads across a water surface to a molecular thin layer, so a droplet of these monomers suspended in a volatile solvent will spread over the water surface to a film that is one molecular unit thin. This loose film of monomers can be compressed by a barrier sweeping across the surface to form a uniform, monolithic film as shown in Figure 2. A glass slide gently dipped through the monomer-water interface will acquire a monolayer coating, which can be thickened by successive dipping. Afterwards, the monomers may be polymerized in place by exposure to radiation. This technique for the fabrication of multilayer polymer samples, the Langmuir-Blodgett method, allows precise control of film thickness and molecular organization. The resultant films have high optical quality and may be suitable for application as waveguides in nonlinear optics experiments (1). The polydiacetylenes, attractive for their extraordinary nonlinear performance, have produced consistent films by this technique.

The diversity of nonlinear responses elicited from

materials by light suggests many different applications. One of the most alluring quests is to replace electronic devices with optical analogues. The optical fiber, bearing information as a modulated light beam, emulates a current-carrying wire with increased information capacity and speed. The installation of optical cables as long telephone lines capitalizes on these assets. At present, however, the optical signal carried on the fiber must be converted to an electrical signal for manipulation and decoding. An all-optical switch, which processes light by light, would circumvent this conversion complexity, without sacrificing the speed of light transport by the signal (2).

An optical switch must function macroscopically much like a mechanical switch: The setting corresponding to "on" must allow light to pass through, while "off" blocks transmission. Current strategies for achieving precise, rapid switching of a light beam are dramatically more sophisticated than Galileo's use of a lantern shutter in his attempt to determine the speed of light (3).

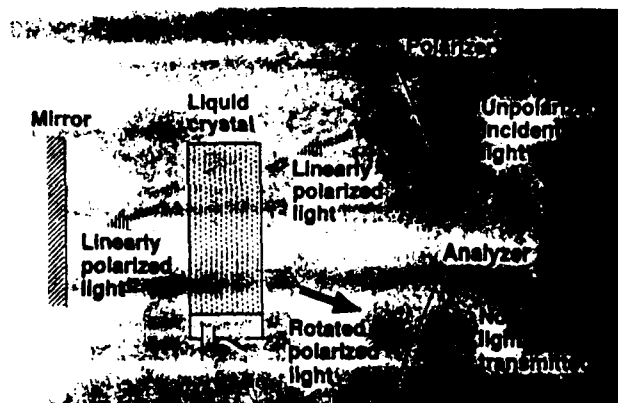
One example for the design of an optical switch regulated solely by fluctuations in the light beam's intensity is provided in Figure 3. A laser beam is directed into a waveguide, in this example a thin channel of a nonlinear material whose index of refraction, higher than the surrounding substrate, confines the light beam within that channel. However, as light propagates by zig-zag reflections down channel A, it slightly exceeds the confines at each reflection. When another waveguide B of high refractive index is situated parallel and very close to A, some of the light from A will spill over into B. Both waveguides will output light: they are coupled together. The waveguide geometry can be so constructed that all the light from A is transferred to B. In this case, a light input in channel A results in light output through B.

A variation in the intensity of the incoming beam alters the index of refraction in the waveguide if it is composed of a nonlinear material. Once the refractive index is increased above a threshold value, the waveguides abruptly decouple, like the flip of a switch. This breakdown of coupling between A and B eliminates light output from B: The transmission of light has been switched (4). The switching speeds (potentially up to  $10^{-13}$  s) for such a device are determined not by waveguide length but by the characteristic response time of the constituent material to changes in optical intensity (5). The polydiacetylenes, with a fast response time of  $\sim 10^{-14}$  s and high nonlinear index in their range of transparent frequencies, are candidate materials for this application.

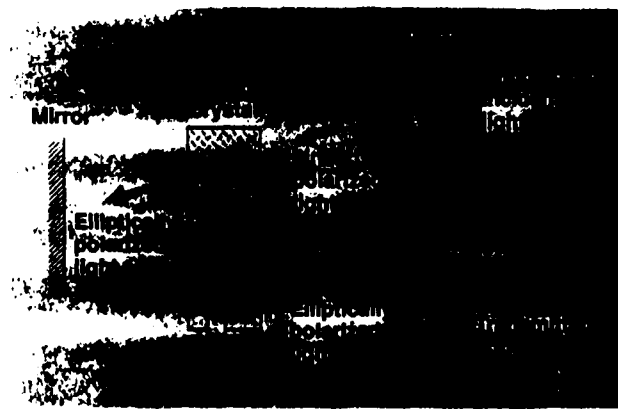
Another mechanism (based on liquid crystals) for switching light is a component of many commercially available image-processing systems. This device, controlled by an applied electric field, screens out light by exploiting its polarization. The oscillation of the electric

vector of linearly polarized light is confined to a plane; if it impinges upon a grating (analyzer) oriented perpendicular to that plane, no light is transmitted. However, when elliptically polarized light falls upon an analyzer, the component parallel to the grating is transmitted. The "off" and "on" states of a liquid crystal light valve are shown schematically in Figures 4 and 5. The long molecules composing the liquid crystal L are initially aligned so that the oscillation plane of linearly polarized light passing through it will be rotated by  $45^\circ$ . Following reflection, the light retraverses L and is rotated further by  $45^\circ$ . It is blocked by the analyzer.

Subsequently, if an electric field is applied across the



**Figure 4.** The "off" state of a liquid crystal light valve. Linearly polarized light, rotated by  $90^\circ$  in two passes through the liquid crystal, is stopped by the analyzer



**Figure 5.** The "on" state of a liquid crystal light valve. Application of an electric field to the liquid crystal transforms the linearly polarized light passing through it to elliptically polarized light. One component of the elliptically polarized light is transmitted by the analyzer

liquid crystal, the long molecules will reorient and the material becomes birefringent. This field-induced orientation of the molecules may transform linearly polarized light to elliptically polarized light. If this effect is attained, one component of the elliptically polarized light will emerge from the analyzer; the device will "switch."

Figure 5. Because this switch depends on a moving part—repositioning of molecules and molecular fragments—it is inherently slower than the preceding examples by several orders of magnitude. Typical response times of several milliseconds to microseconds, however, by small fields are adequate to achieve switching (6).

The ability to transform the frequency of light from one regime to another (e.g., from visible to ultraviolet) has evident practical import. A device that performs this operation is schematically simple: a single crystal. However, the crystal's orientation with respect to the laser beam is critical.

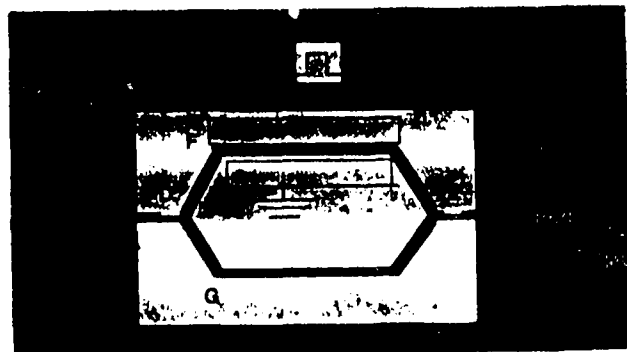
Detection of the harmonic (i.e., the multiple of the incident frequency) is only possible when the velocities of the incident light and the harmonic along the chosen crystal axis are matched. Urea ( $\text{NH}_2\text{CONH}_2$ ) and MNA crystallize in forms lacking a center of symmetry to produce an efficient second harmonic signal.

A continuous, uniform light beam is not useful for information transfer. However, any of its observable properties, including intensity, frequency, phase, or polarization, may be deliberately modified to impart an information content to the beam. A modulator, a device that performs this function, is at the crux of any system based on optically transmitted signals. The modulator transposes coded information from an electrical, acoustic, or magnetic signal onto a light beam.

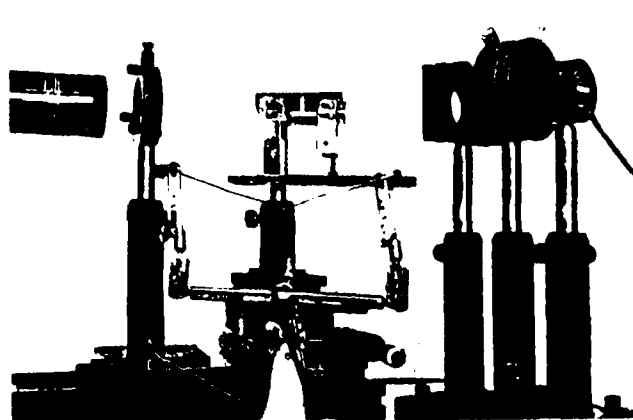
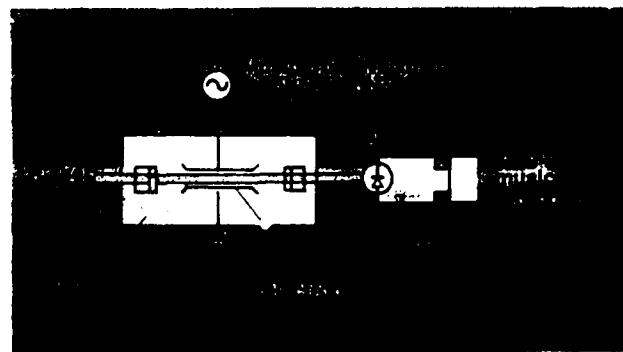
One popular scheme for modulating light, the Mach-

Zender interferometer, consists of a waveguide or a transparent material split into channels that recombine (Figure 6). A collimated beam of light enters the device at C. It is divided by the waveguide into two beams, ideally of equal amplitude, at D. The beam in channel F is subjected to a modulating signal (electric field, acoustic field, etc.). The index of refraction in channel F changes, creating a discrepancy between the speed of light in the two channels. As a result the two initially coherent beams run out of synchronization with each other; their phases are mismatched at E and the beams partially cancel. The difference in phase of the two beams at E is proportional to the induced change in index of refraction in F. By regulating the index change, the phase difference at E can be controlled; thus light from the two channels will totally cancel in the device output. This device is, in principle, an electronically controlled switch. Switching rates of up to tens of picoseconds ( $10^{-11}$  s) are possible (7-9).

In a Mach-Zender device, the waveguide channels are fabricated from a material that responds to an applied electric field with a pronounced change in index of refraction. A DANS guest-host system could be prepared



**Figure 6. A Mach-Zender Interferometer.** The light input at C is divided at D into two channels: F and G. The material in channel F is subjected to an electric field, which changes its index of refraction. The phase of light that traversed channel F does not match the phase of light from channel G. When the two beams are combined at E, their phases partially cancel, resulting in a reduced output.



**Figure 7. Diagram of a demonstration of organic nonlinear materials designed by the Advanced Photonics Division of Hoechst Celanese and a photograph of the apparatus.** NL O = nonlinear optics

as a spin-coated film within the channel. If the sample is heated beyond its glass transition temperature, an electric field can align the DANS molecules in the desired direction within the channel. Upon cooling, this orientation will be frozen in place. Alternatively, organic materials could be processed into waveguide geometries by several methods including the Langmuir-Blodgett technique, or by growing single crystals from solution or from melt.

The optical devices described above already exist, either as prototypes or as manufactured components. The Advanced Photonics unit of Hoechst Celanese based in Summit, N.J. (10), has designed the effective demonstration of its nonlinear polymeric materials shown in Figure 7. The audio signal from a Walkman radio applies a changing electrical voltage between two electrodes separated by a layer of nonlinear material. The material's index of refraction changes in step with variations in the applied field, thus creating a phase difference between two oscillation modes of light traveling in the layer. This optical phase difference is converted at the photodetector to a modulated electrical signal that, when fed to a loudspeaker, reproduces the original music. The polymer has facilitated the translation of a signal from audio to electrical to optical and back to electrical and audio without compromising its fidelity. An ordinary listener, without specialized knowledge, can appreciate the practicality of this set of transformations for

communications applications by hearing the audio output of the device.

Several other companies are marketing products that incorporate the unique properties of nonlinear organic materials. Liquid crystal devices and materials are available from Displaytech Inc. (11). Cleveland Crystals (12) supplies an extensive range of crystals grown in their labs for scientific and industrial applications. Their stock includes both inorganic and organic crystals with nonlinear optical properties. In addition they have facilities for the fabrication and testing of laser-optic components such as harmonic generators.

Preliminary studies of organic materials have demonstrated their exceptional nonlinear response to light. Empirically based inference on how the form of a molecule relates to its function may guide the design of new organics, optimized to perform a specific role in this developing technology.

### Conclusion

Our picture of the interaction between light and matter has been enriched in detail by the retinue of new nonlinear phenomena first manifested by laser light. The effect is mutually induced: the electric field of light distorts molecular structure, which in turn alters some features of the beam. The efficiency of an interaction at producing nonlinear effects can be finely tuned by incremental



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adjustments in the material. Organic material, whose structure—like a microscopic Lego set—can be remodelled at will, may merit prominence in the effort to devise components based on the physics of nonlinear optics.

The novel optical behavior of organic materials could invert the hierarchy of materials employed in communications technology. Engineering plastics have seen service primarily as passive components: housing for computers, packaging for microelectronic devices, and insulators for current-carrying cables. Silicon-based materials have been at the top of the hierarchy, directly engaged in the conduct and manipulation of information. In the future molecularly engineered plastics may constitute the key active components, such as modulators and switches, that process the crucial decisions of our complex world. Further, just as the laser engendered a branch of physics, the tailor-made materials themselves

may reveal new, unexpected physical and chemical phenomena.

#### References

- (1) Agarwal, V. K. *Phys. Today* 1988, 41(6), 40-6.
- (2) Glass, A. M. *MRS Bull.* 1988, 13(8), 16-20.
- (3) Galileo, G. *Two New Sciences Including Centres of Gravity, Force of Percussion, Drake's Triangle*, University of Wisconsin Press, Madison, 1964, 49-50.
- (4) Tamir, T. In *Integrated Optics*, Tamir, T., Ed., Springer-Verlag, New York, 1982, 83-137.
- (5) Smith, P. W. *IEEE Circuits and Devices*, May 1987, 9-14.
- (6) Knight, G. R. In *Optical Information Processing: Fundamentals*, Lee, S. H., ed., Springer-Verlag, New York, 1981, 114-9.
- (7) Henner, J. M. In *Integrated Optics*, op. cit., 139-200.
- (8) Hunsperger, B. G. In *Integrated Optics: Theory and Technology*, Springer-Verlag, New York, 1985, 135-6.
- (9) Becker, R. A. *MRS Bull.* 1988, 13(5), 21-3.
- (10) Advanced Photonics, Hoechst Celanese Corporation, 86 Morris Avenue, Summit, NJ 07901.
- (11) Displaytech Inc., P.O. Box 7246, Boulder CO 80306.
- (12) Cleveland Crystals, Inc., P.O. Box 17157, Cleveland OH 44117.

#### NOW WE KNOW

Nature uses large molecules to bring together many different functions in one place and make them work together. That's macromolecular assembly. And in so doing, nature does quite literally, and actually chemically, convert food into thought.

Jacqueline K. Barton  
Columbia University

We have not inherited this land from our ancestors;  
rather we have borrowed it from our children.

Kenyan proverb

#### GET OUT OF THAT RUT

Oscar Wilde said, "Consistency is the last refuge of the unimaginative." So stop getting up at 6:05. Get up at 5:06. Walk a mile at dawn. Find a new way to drive to work. Switch chores with your spouse next Saturday. Buy a wok. Study wildflowers. Stay up alone all night. Read to the blind. Start counting brown-eyed blondes and blonds. Subscribe to an out-of-town paper. Canoe at midnight. Don't write to your congressman, take a whole scout troop to see him. Learn to speak Italian. Teach some kid the thing you do best. Listen to two hours of uninterrupted Mozart. Take up aerobic dancing. Leap out of that rut. Savor life. Remember, we only pass this way once.

